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# **The rate of water vapor evaporation from ice substrates in the presence of HCl and HBr: Implications for the lifetime of atmospheric ice particles**

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## Abstract

Using a multidagnostic approach the rate  $R_{ev}$  or flux  $J_{ev}$  of evaporation of  $H_2O$  and its condensation,  $k_{cond}$ , on a  $1\mu m$  thick ice film have been studied in the temperature range 190 to 240 K as well as in the presence of small amounts of HCl and HBr that left the vapor pressure of  $H_2O$  on ice unchanged. The resulting Arrhenius expressions with RT in kcal mol<sup>-1</sup> for pure ice are  $J_{ev} = 1.6 \cdot 10^{28 \pm 1} \cdot \exp\left(\frac{-10.3 \pm 1.2}{RT}\right)$  [molec cm<sup>-2</sup> s<sup>-1</sup>],  $k_{cond} = 1.7 \cdot 10^{-2 \pm 1} \cdot \exp\left(\frac{+1.6 \pm 1.5}{RT}\right)$  [s<sup>-1</sup>], in the presence of an HCl mole fraction in the range  $3.2 \cdot 10^{-5} - 6.4 \cdot 10^{-3}$ :  $J_{ev} = 6.4 \cdot 10^{26 \pm 1} \cdot \exp\left(\frac{-9.7 \pm 1.2}{RT}\right)$  [molec cm<sup>-2</sup> s<sup>-1</sup>],  $k_{cond} = 2.8 \cdot 10^{-2 \pm 1} \cdot \exp\left(\frac{+1.5 \pm 1.6}{RT}\right)$  [s<sup>-1</sup>], and an HBr mole fraction smaller than  $6.4 \cdot 10^{-3}$ :  $J_{ev} = 7.4 \cdot 10^{25 \pm 1} \cdot \exp\left(\frac{-9.1 \pm 1.2}{RT}\right)$  [molec cm<sup>-2</sup> s<sup>-1</sup>],  $k_{cond} = 7.1 \cdot 10^{-5 \pm 1} \cdot \exp\left(\frac{+2.6 \pm 1.5}{RT}\right)$  [s<sup>-1</sup>]. The small negative activation energy for  $H_2O$  condensation on ice points to a precursor mechanism. The corresponding enthalpy of sublimation is  $\Delta H_{subl} = E_{ev} - E_{cond} = 11.9 \pm 2.7$  kcal mol<sup>-1</sup>,  $\Delta H_{subl} = 11.2 \pm 2.8$  kcal mol<sup>-1</sup>, and  $\Delta H_{subl} = 11.7 \pm 2.8$  kcal mol<sup>-1</sup> whose values are identical within experimental uncertainty to the accepted literature value of 12.3 kcal mol<sup>-1</sup>. Interferometric data at 633 nm and FTIR absorption spectra in transmission support the kinetic results. The data are consistent with a significant lifetime enhancement for HCl- and HBr-contaminated ice particles by a factor of 3–6 and 10–20, respectively, for submonolayer coverages of HX.

## 1. Introduction

Heterogeneous reactions occurring on the surface of polar stratospheric clouds (PSC's) are known to play an important role in controlling the abundance of  $O_3$  in the polar stratosphere by converting hydrogen halide reservoir species HX (X=Br,Cl) into photolytically active halogens (Solomon et al., 1986; Tolbert et al., 1987; Wennberg et al., 1996; WMO Report, 1998). In addition, recent studies indicate that Cirrus cloud ice

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particles near the tropopause may act as substrates for heterogeneous reactions akin to PSC's with a similarly high efficiency (Borrmann et al., 1996; Solomon et al., 1997). Contrary to the polar stratosphere where PSC's are recurrent or persistent enough for complete heterogeneous processing of halogen containing reservoir molecules, the situation in the midlatitude upper troposphere is quite different. Natural or aviation-induced Cirrus clouds have a limited lifetime during which heterogeneous processing may occur. Borrmann et al. have assumed an average cloud lifetime of only 20 min. which nevertheless led to a significant predicted impact on atmospheric chemistry. Therefore, the evaporative lifetime of Cirrus ice particles and the impact of atmospheric trace gas adsorbates such as HX on this lifetime are important parameters controlling the extent of heterogeneous processes.

For several years, a considerable number of studies on the kinetics of evaporation of H<sub>2</sub>O on ice has been performed. Some of these studies have focused on the temperature dependence of the rates of evaporation and condensation of H<sub>2</sub>O on pure ice using different techniques (Haynes et al., 1992; Brown et al., 1996; Chaix et al., 1998; Fraser et al., 2001). Others have mainly revealed the impact of trace gases of atmospheric importance on the evaporation rates, such as HNO<sub>3</sub> (Warshawsky et al., 1999), HCl or HBr (Hudson et al., 2001). The main result of these studies is the observation of the decrease of the rate of evaporation of H<sub>2</sub>O ( $R_{ev}$ ) on doped ice compared to  $R_{ev}$  on pure ice to variable extents. In this work both the kinetics of condensation ( $k_c$ ) and evaporation ( $R_{ev}$ ) have been measured under the same experimental conditions which has to our knowledge not been done before. The emphasis of the present work lies in the experimental separation of  $k_c$  and  $R_{ev}$  in order to obtain thermochemical closure with the H<sub>2</sub>O vapor pressure over ice which puts a constraint on the rate separation.

Several studies address the direct investigation of the condensed phase of H<sub>2</sub>O in order to characterize the ice substrate using FTIR spectroscopy. Thus, the investigation of the IR absorption spectrum of pure ice has been undertaken (Schrivier-Mazzuoli et al., 2000) in order to spectroscopically characterize the ice structure, as well as the impact of HNO<sub>3</sub>, HCl and HBr deposition (Ritzhaupt et al., 1990; Delzeit et al., 1993;

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Koehler et al., 1993; Horn et al., 1997; Dominé et al., 2001; Zondlo et al., 2000; Hudson et al., 2001). This led to the discovery of different surface species owing either to the formation of stoichiometric hydrates or amorphous mixtures. Because most of the aforementioned experiments have been performed under UHV conditions, they have been limited to temperatures well below 220 K which is the characteristic temperature of the tropopause and is of interest here. Therefore, we have extended the temperature range to 240 K in the present work.

## 2. Experimental apparatus

The present experiment is a stirred flow reactor equipped with triple diagnostics. It allows FTIR spectroscopic characterization of the ice substrate in transmission as well as observation of the changes of the condensed phase thickness based on HeNe interferometry at 632.8 nm. In addition, a residual gas mass spectrometer enables the monitoring of the partial pressures above the HX/Ice condensate. The experimental apparatus consists of a stainless steel cylindrical reactor of volume  $V_r = 1750$  or  $2450$  cm<sup>3</sup>, equipped with various inlets and electrical and optical feedthroughs including two 2" diameter NaCl windows to enable FTIR monitoring of the HX/Ice condensate. The reactor is pumped at the bottom by a turbomolecular-pump (VARIAN Turbo-300VHT,  $250 \text{ l s}^{-1} \text{ N}_2$ ) through a 6" diameter gate valve that is closed during experiment, thus isolating the upper (reactor) and lower chamber, the latter of which is monitored by a residual gas mass spectrometer (BALZERS Prisma QMS200). The liquid nitrogen cryostat, mounted on top of the reactor and externally heated using electrical cartridge heaters allows for accurate temperature control of the NaCl or Si optical window serving as the substrate for ice deposited from the vapor phase in the range  $100 \geq T/K \geq 250$  ( $\pm 1$  K). The ice temperature is periodically checked against the vapor pressure of H<sub>2</sub>O over ice (Marti et al., 1993) using a type T thermocouple and a Baratron absolute pressure gauge (220-AHS). We would like to stress that in contrast to most other cryostats presently in use the Si window of  $0.78 \text{ cm}^2$  cross section used as the substrate for the

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ice films is the only cold part of the chamber exposed to the gas phase (see Fig. 1). This has been checked in numerous experiments by correlating the loss of H<sub>2</sub>O vapor by monitoring the pressure change in the Teflon (FEP)-coated calibrated volume used as a reservoir for the injection of H<sub>2</sub>O molecules into the reactor with the number of molecules deposited on the Si window by monitoring the optical density in the IR spectral region and the integrated MS signal resulting from the evaporation of the ice film.

Three types of measurements have been performed in the present experiment. The first is based on the use of a residual gas MS which is connected to the upper chamber both by a 6" diameter gate valve and a calibrated leak whose rate constant for effusion of H<sub>2</sub>O and HCl are  $k_{\text{esc}}(\text{H}_2\text{O})=0.055 \text{ s}^{-1}$  and  $k_{\text{esc}}(\text{HCl})=0.043 \text{ s}^{-1}$ , respectively. These values have been obtained from the evaluation of the exponential decrease of the pressure in the reactor measured using a 1 mbar full scale Baratron gauge (MKS Baratron pressure transducer Type 220AHS) when it is set from static to stirred flow condition by opening the calibrated leak valve. This leak allows the use of the reactor either under static conditions with the calibrated leak closed or as a stirred flow reactor with the leak valve open (see Fig. 1). It operates from the free molecular flow regime to the transition region up to a mbar or so of total pressure. In this latter configuration the range of water partial pressures ( $P_{\text{H}_2\text{O}}$ ) in the upper chamber ranges from  $10^{-4}$  to 1 mbar and is measured using the 1 Torr full scale Baratron gauge. The gas composition is continuously measured using the MS with the calibrated leak valve open.

The second diagnostic is based on a Fourier Transform Infrared Spectrometer (BIO-RAD FTS-575C) used in transmission across the Si window. It characterizes the composition changes of the condensed phase, which corresponds 1:1 to changes of the gas phase composition as the optical window is the coldest point of the whole reactor owing to extensive thermal insulation of the cryostat but the optical window using a tightly fitted PTFE sleeve. Therefore, any change in the optical density of the deposited film due to evaporation or condensation in the static cryostat system is accompanied by a change in  $P_{\text{H}_2\text{O}}$  which can be monitored using either the partial pressure (MS) or

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the absolute pressure gauge.

The third diagnostic technique is based on He-Ne interferometry used to monitor changes of the thickness of the ice deposit with time. In such a configuration, the change of the thickness  $d_i$  is given by the relation

$$d_i = N_i \frac{\lambda}{2} \frac{1}{\sqrt{n_i^2 - \sin^2 \theta}} \quad (1)$$

where  $d_i$  is the total change in thickness of the ice film,  $N_i$  the number of observed fringes,  $\lambda = 632.8$  nm the wavelength of the He-Ne laser,  $n_i$  the refractive index of vapor deposited ice set to  $n_i = 1.3$  and independent of  $T$  in the range 180–220 K (Berland et al., 1995), and  $\theta = 12^\circ$ , the angle between the normal to the ice surface and the incident He-Ne beam. Using the appropriate parameters for the present cryostat one obtains  $d_i = 246 \times N_i$  nm which indicates a difference  $d_i$  in ice thickness of 246 nm between the homologous points of two adjacent interference fringes. This leads to the number of water molecules deposited on the substrate of  $N_{H_2O} = 6.2 \times 10^{17} \times N_i$  with the density of ice being constant and equal to 0.93 (Berland et al., 1995) in the range 180 to 220 K. The ice film is grown under static conditions by deposition from water vapor using bidistilled water at a typical rate of  $10^{17}$  molecule  $s^{-1}$  by flowing  $H_2O$  vapor across a gas dosing tube directed towards the optical substrate. The mean ice thickness is approximately  $1 \mu m$  before HCl deposition starts.

The measurement of the dose of HCl or HBr on the deposited ice film follows a two-pronged strategy which consists of (1) establishing the absolute flow rate of HX admitted into the cryostat chamber using MS signals under stirred flow conditions, and (2) integrating the loss of HCl by adsorption from the gas phase in the presence of the ice film when the HCl lost from the gas phase has been condensed on the optically diagnosed ice film. Step (1) involves monitoring the MS signal at  $m/e = 36$  for HCl and  $m/e = 82$  for HBr, with the gate valve closed and the calibrated leak open thus enabling gas phase monitoring on-line under stirred flow condition. Previously, the MS signal intensities for HCl had been calibrated thus leading to a 1:1 relationship between the

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MS signals and the HCl concentration in the chamber. Using the known values of  $k_{\text{esc}}$  for HCl, the measurement of the partial pressure of the trace gas using the Baratron gauge in the cryostat chamber or the corresponding MS signal of HCl leads to the absolute flow rate in  $\text{molec s}^{-1}$  according to Eq. (2):

$$\text{Flow rate} = \frac{PV}{RT} k_{\text{esc}} = [\text{H}_2\text{O}] V k_{\text{esc}} = C V k_{\text{esc}} P, \quad (2)$$

where C is the conversion factor between partial pressure of  $\text{H}_2\text{O}$  and water concentration in  $\text{molec Torr}^{-1} \text{cm}^{-3}$  ( $3.2 \cdot 10^{16}$  and  $2.9 \cdot 10^{16}$  for configurations 1 and 2, respectively, and displayed in Table 1), P the pressure of HCl in Torr, V the volume of the reactor and  $k_{\text{esc}}$  the rate of effusion of HCl through the calibrated leak in  $\text{s}^{-1}$  (see Table 1 for detailed information). Moreover, as the glass inlet used for trace gas injection into the upper chamber is equipped with a micrometer dosing valve (Swagelok double pattern low-pressure metering valve with vernier handle Type SS-SS2-D-TVVH) located between the calibrated volume used as a reservoir for HX and the inlet dosing tube, we have calibrated this valve by establishing the correspondence between the size of its aperture and the resulting MS signal, thus leading to an absolute calibration of the flow rate of HX molecules injected versus the aperture size of the micrometer dosing valve. Step (2) consists of integrating the absolute flow of HCl that was condensed onto the ice film in order to assess the HCl dose. As the window of the cryostat exposed to the gas is known to be the only part that is at low temperature during the experiment, the difference of the integrals of the MS signal of HX with the optical substrate at ambient temperature (no ice) and in the presence of an ice film, enables the evaluation of the absolute number of molecules deposited onto the ice. Figure 2 displays a typical experiment performed in order to obtain an absolute calibration of the HCl dose.

The smallest measurable MS signal level at  $m/e=36$  within the S/N ratio of our apparatus is on the order of  $3 \times 10^{-13} \text{ A}$  with a rise time of nearly 10 s. This leads to an estimate for the smallest measurable amount of HCl deposited on the optical substrate of  $2 \cdot 10^{12}$  molecules corresponding to  $3 \cdot 10^{-3}$  of a formal monolayer using a calibration factor for the MS signal of  $6.25 \times 10^{23} \text{ molec s}^{-1} \text{ A}^{-1}$ . The lowest achievable deposition

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rate was  $2 \cdot 10^{11}$  molec s<sup>-1</sup> and the lowest detectable partial pressure of HCl monitored by residual gas MS was of the order of  $6 \cdot 10^{-8}$  Torr. We have estimated that owing to the very small gas phase density of HCl in the presence of an ice film of typically  $8 \cdot 10^{-8}$  Torr the adsorption of gas phase HCl would take a time exceeding the typical duration of the present experiments. We have therefore ignored the deposition rate of HCl onto the ice sample under HCl background conditions afforded by the maximum pumping speed of the vacuum chamber. Dosing of the ice is performed either by the deposition of the trace gas under static conditions by backfilling the reactor volume with a measured amount of trace gas or by directed deposition of pure HCl onto ice across the same dosing tubes used for the deposition of the ice film. No significant differences in the kinetic results have been observed when comparing the backfilling with the directed deposition technique. For HBr the present experimental setup does not allow quantitative dosing experiments because the PTFE insulation apparently irreversibly adsorbs small quantities of HBr. However, the used deposition settings for HBr were identical to the ones used for HCl allowing the estimation of upper limits for the concentration of HBr.

### 3. Results

Both the rate of evaporation  $R_{\text{ev}}$  and the uptake coefficient  $\gamma$  of H<sub>2</sub>O vapor uptake on ice have been measured between 200 and 240 K for pure ice and in the presence of known amounts of HX (X=Cl or Br) according to the net reaction:



with  $\gamma = k_{\text{cond}} / \omega$ , where  $\omega$  is the collision frequency of H<sub>2</sub>O with the ice film (see Table 1). The separation of the rate of evaporation and condensation was enabled by using a method which consisted of the consecutive use of the reactor in the static and the stirred flow mode. By measuring  $P_{\text{eq}}$ , the equilibrium H<sub>2</sub>O vapor pressure in the

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reactor (upper chamber) under static condition, and  $P_{ss}$ , its corresponding steady state partial pressure under stirred flow condition,  $R_{ev}$  and  $k_{cond}$  were calculated using the following equations:

$$P_{eq} = \frac{R_{ev}}{k_{cond}} \times RT \quad P_{ss} = \frac{P_{eq}}{\frac{k_{esc}}{k_{cond}} + 1} \quad (4)$$

5 In all these experiments ice was deposited at 190 K at a rate of  $10^{17}$  molec  $s^{-1}$  and heated to the desired temperature after deposition. Both  $P_{eq}$  and  $P_{ss}$  have been corrected for the fact that the colliding gas, namely water vapor, was at ambient or slightly higher temperature as it is controlled by the temperature of the chamber walls whereas the target consisting of the ice film deposited on the optical support was at low temperature. Under those conditions both the pressures,  $P_{eq}$  and  $P_{ss}$ , as well as  $[H_2O]$  are related to the measured values by both the temperature of the cold target and the chamber walls at ambient temperature. The correction procedure valid for the molecular flow regime is explained in more detail in the Appendix.

15 The protocol for the deposition of ice leading to samples of typically 1  $\mu m$  thickness was kept the same throughout the present study. The deposition temperature of 190 K was deliberately chosen so as to lead to the formation of thermodynamically stable polycrystalline ice of hexagonal  $I_h$  crystal structure thus minimizing the occurrence of mixtures with cubic and amorphous phases that are metastable at 190 K. A mixture of ice phases may lead to a H-bonding environment that is different compared to the thermodynamically stable pure ice phase  $I_h$  crystal structure as has been shown by Schaff and Roberts (1996) using FTIR reflection-absorption spectroscopy. In addition, we may exclude the presence of a significant degree of porosity in the present ice films as shown by Keyser et al. (1992). We have therefore chosen an ice deposition protocol that should always lead to a homogeneous film of thermodynamically stable  $I_h$  crystal structure irrespective of the temperature of the film used for further investigations.

25 A known quantity (dose) of HX was subsequently deposited on the pure ice film, and both the equilibrium vapor pressure  $P_{eq}$  of  $H_2O$  as well as its steady state value

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$P_{ss}$  were measured using the absolute pressure gauge or the MS signal for  $P_{ss}$ . This allowed the determination of  $R_{ev}$  and  $\gamma$  of  $H_2O$  in the presence of HX in comparison with pure ice. The number of HCl molecules adsorbed on the ice was in the range  $10^{13}$  –  $10^{15}$  molecules corresponding to 0.01 to 1 formal monolayer with an upper limit of the HCl deposition rate of  $10^{14}$  molec  $s^{-1}$ . For HBr the number of molecules adsorbed and the deposition rate are similar to HCl as only limiting values can be given (see above). During the measurement of  $P_{ss}$  of  $H_2O$  no HX desorption has been observed while  $H_2O$  was evaporating from the ice, and a change in  $m/e=36$  and 82 for HCl and HBr, respectively, was only observable during the evaporation of the last few tens of nm as observed by simultaneous monitoring of the change in thickness of the ice deposit and the gas phase composition using HeNe interferometry and MS, respectively. One must keep in mind that steady state conditions for  $H_2O$ ,  $P_{ss}$ , were attained once a significant fraction of the ice sample evaporated. The remaining thickness corresponded to the last few hundred nanometers of ice between points **C** and **D** of the HeNe interferogram displayed in Fig. 3. Thus the mean HCl mole fraction in the remaining ice film was in the range  $3.2 \cdot 10^{-5}$  to  $6.4 \cdot 10^{-5}$  for a dose of  $10^{13}$  adsorbed HCl molecules, and between  $3.2 \cdot 10^{-3}$  and  $6.4 \cdot 10^{-3}$  for a dose of  $10^{15}$  adsorbed HCl. The latter case corresponds to the situation between points **C** and **D** of the displayed HeNe interferogram.

The kinetic results are shown in Figs. 4 and 5 which display  $J_{ev}$ , the evaporative flux and  $\gamma$ , the uptake coefficient. The rate  $R_{ev}$  and flux  $J_{ev}$  of evaporation are connected through the relationship  $J_{ev}=R_{ev}/(A_s/V)$ , where  $(A_s/V)$  is the surface-to-volume ratio of the used experimental arrangement (see Table 1). It is important to point out that in the presence of the dose of adsorbed HX in the range given above, the measured equilibrium vapor pressure  $P_{eq}$  of  $H_2O(g)$  is that over pure ice and therefore independent of the doses of HX over the range explored. Figure 4 shows the decrease of  $J_{ev}$  in the presence of HCl relative to that of pure ice by a factor of 3 to 6 at doses smaller than  $10^{15}$  molec  $cm^{-2}$  corresponding to one formal monolayer or less of HCl. The uptake coefficient  $\gamma$  displayed in Fig. 5 undergoes the same change as  $J_{ev}$  owing to the constraint that the measured  $P_{H_2O}$  is that of pure ice. This decrease in  $J_{ev}$  and  $\gamma$  depends

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upon the number of HCl molecules deposited on the surface of the ice, but stays constant for amounts larger than  $10^{14}$  molecules of HCl adsorbed on ice as displayed in Fig. 6. It shows the HCl dose dependence of  $J_{\text{ev}}$  together with a discontinuity around  $6 \cdot 10^{13}$  of deposited HCl molecules which corresponds to a mole fraction for HCl in ice between  $1.9 \cdot 10^{-4}$  and  $3.8 \cdot 10^{-4}$ . It seems that for doses of deposited HCl up to  $1 \cdot 10^{14}$ ,  $J_{\text{ev}}$  stabilizes around  $5 \cdot 10^{16}$  molec  $\text{cm}^{-2} \text{s}^{-1}$  which is the value displayed in Fig. 4 at 210 K. However for larger doses of HCl  $J_{\text{ev}}$  and  $\gamma$  continue to decrease. Figures 4 and 5 display all values obtained in this work including the ones at very large HCl doses (inverted triangles in Figs. 4 and 5).

The energy of activation for the flux of evaporation,  $J_{\text{ev}}$ , and the rate constant for condensation,  $k_{\text{cond}}$  of  $\text{H}_2\text{O}$  from pure ice is calculated to be  $E_{\text{ev}} = 10.3 \pm 1.2 \text{ kcal mol}^{-1}$  and  $E_{\text{cond}} = -1.6 \pm 1.5 \text{ kcal mol}^{-1}$ , respectively, leading to the Arrhenius expression  $J_{\text{ev}} = 1.6 \cdot 10^{28 \pm 1} \cdot \exp\left(\frac{-10.3 \pm 1.2}{RT}\right) [\text{molec cm}^{-2} \text{s}^{-1}]$  and  $k_{\text{cond}} = (1.7 \cdot 10^{-2 \pm 1}) \cdot \exp\left(\frac{+1.6 \pm 1.5}{RT}\right) [\text{s}^{-1}]$  for the range 200 to 240 K and  $RT$  in kcal  $\text{mol}^{-1}$ .

For HCl doped-ice the values are  $E_{\text{ev}} = 9.7 \pm 1.2 \text{ kcal mol}^{-1}$  and  $E_{\text{cond}} = -1.5 \pm 1.6 \text{ kcal mol}^{-1}$  leading to  $J_{\text{ev}} = 6.4 \cdot 10^{26 \pm 1} \cdot \exp\left(\frac{-9.7 \pm 1.2}{RT}\right) [\text{molec cm}^{-2} \text{s}^{-1}]$  and  $k_{\text{cond}} = (2.8 \cdot 10^{-2 \pm 1}) \cdot \exp\left(\frac{+1.5 \pm 1.6}{RT}\right) [\text{s}^{-1}]$  for the range 200 to 240 K.

In the presence of HBr, the decrease of  $J_{\text{ev}}$  is more important than for HCl and  $J_{\text{ev}}$  is almost 20 times smaller than on pure ice for similar estimated doses of HBr. This led to an activation energy of  $\text{H}_2\text{O}$  evaporation and condensation from HBr-doped ice of  $E_{\text{ev}} = 9.1 \pm 1.2 \text{ kcal mol}^{-1}$  and  $E_{\text{cond}} = -2.6 \pm 1.6 \text{ kcal mol}^{-1}$ , respectively, leading to  $J_{\text{ev}} = 7.4 \cdot 10^{25 \pm 1} \cdot \exp\left(\frac{-9.1 \pm 1.2}{RT}\right) [\text{molec cm}^{-2} \text{s}^{-1}]$  and  $k_{\text{cond}} = (7.1 \cdot 10^{-5 \pm 1}) \cdot \exp\left(\frac{+2.6 \pm 1.5}{RT}\right) [\text{s}^{-1}]$  in the range 200 to 240 K. Following these results, the decrease of the pre-exponential factor in  $J_{\text{ev}}$  is responsible for the most part for the change of the rate of evaporation of  $\text{H}_2\text{O}$  thus leaving the exponential factor unchanged within experimental uncertainty.

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Observations of the condensed phase in the absence and the presence of HCl have also been performed using HeNe interferometry simultaneously with MS and FTIR measurements. Figure 3 shows the decrease of the thickness of a 1  $\mu\text{m}$  thick slab of pure and HCl-doped ice at 190 K with time. First, the ice film is grown under static conditions, and is subsequently doped with  $10^{15}$  molecules of HCl or HBr. The decrease in the net rate of  $\text{H}_2\text{O}$  evaporation of the 1  $\mu\text{m}$  thick ice film in the presence of  $10^{15}$  deposited HCl molecules corresponding to less than 2 monolayers amounts to a factor of 5 to 6 compared to pure ice once steady state is achieved between points **C** and **D** and maintained to point **E**. This is also the time period during which  $P_{\text{ss}}$  (Eq. 4) has been measured. The portion of the interferogram between  $t=100$  and 300 s in Fig. 3 containing points **C** and **D** describes a sinusoidal change of the photodiode signal which in turn corresponds to a linear change of thickness with time according to Eq. (1). This result is in good agreement with the decrease of  $R_{\text{ev}}$  observed in the presence of HCl discussed above, albeit not directly comparable. The observation of the condensed phase implies a **net** change, that is the difference between evaporation and condensation rate whereas the gas phase measurement results in the separation of the net process in terms of  $R_{\text{ev}}$  and  $k_{\text{cond}}[\text{H}_2\text{O}]_{\text{ss}}$ . The net change observed interferometrically is somewhat less than the change based on  $R_{\text{ev}}$  alone within a factor of two as condensation of  $\text{H}_2\text{O}$  onto the remaining ice film counteracts the decrease of the thickness owing to  $R_{\text{ev}}$ .

One may note that the spacing between the interferometric fringes is gradually becoming larger which corresponds to a decrease of the net rate of evaporation starting around  $t=50$  s as shown in Fig. 3, point **B**, where  $1.5 \cdot 10^{18}$  molecules of  $\text{H}_2\text{O}$  still remain in the ice film compared to  $2.5 \cdot 10^{18}$  at the beginning of the evaporation. As no desorption of HX from the film was observed using MS, we therefore claim that the amount of HX adsorbed on the ice film is responsible for this change of  $J_{\text{ev}}$  as discussed above. At first only the  $\text{H}_2\text{O}$  molecules that are not influenced by the presence of HX are evaporating at the characteristic rate of pure ice which corresponds to the portion of the interferogram of Fig. 3 between points **A** and **B**. Between points **B** and

**E** of the interferogram the decrease of the rate of evaporation of  $\text{H}_2\text{O}$  is due to the effect of HX on the water molecules making up the remainder of the ice substrate. The presence of HX is being felt more strongly with time as the mole fraction of HX in ice becomes more important owing to the fact that only  $\text{H}_2\text{O}$  but no HCl is desorbing. This results in an upper limit value of  $\chi_{\text{HCl}} = 1.2 \cdot 10^{-2}$  at point **E** in Fig. 3. From point **E** of the interferogram to the end of the evaporation of the film we have observed HCl in the gas phase using MS detection.

Figure 8 presents a cartoon describing these processes where **1** corresponds to the composition of the substrate within the time period between **A** and **B** of the interferogram, **2** to the period between **B** and **C** and **3** to the period between **C** and **E**.

Table 2 displays some typical observations of the temporal evolution of the HeNe interferogram for different doping condition of the ice film under stirred flow conditions. Case (a),(b) and (c) refer to one experimental configuration, whereas cases (a') and (b') differ from the former by a change of the calibrated leak. The comparison between (a) and (b), on the one hand, and (a') and (b') on the other hand illustrates the conclusions cited above concerning the change in the net rate of  $\text{H}_2\text{O}$  evaporation from ice in the presence of HCl. In the cases (b), (c) and (b') corresponding to HCl doping the evaporation rate for 50 to 75% of the film thickness is that of pure ice and therefore not affected by the presence of  $1 \cdot 10^{15}$  HCl molecules. Cases (c) and (b') make for an interesting comparison. The stable hydrate  $\text{HCl} \cdot 6\text{H}_2\text{O}$  (case (b')), whose formation will be discussed below, slows down  $R_{\text{ev}}$  significantly, say by a factor of less than 20 corresponding to 600 vs. 35s which is the time needed to evaporate an ice film thickness of 246 nm corresponding to one interference fringe of the HeNe interferogram. However, the crystalline hydrate (case (b')) extends just over one fringe at the used HCl dose whereas the presence of the amorphous hydrate (case (c)) affects 50% of the sample thickness as it is apparently distributed in a more diffuse manner across the ice sample. In contrast its presence affects the  $\text{H}_2\text{O}$  evaporation rate to a lesser extent corresponding to a decrease of a factor between 2 and 3. We would like to stress, however, that the resolution of the HeNe interferogram is too crude in order to draw

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quantitative conclusions in the present case. We just underline the qualitatively similar conclusions between the interferometric and the quantitative kinetic results discussed above. For HBr doping, the decrease in the net rate of evaporation as observed from the corresponding interferogram is on the order of 30 to 40 for HBr levels similar to HCl which is within a factor of two of the results on  $R_{\text{ev}}$  discussed above (Fig. 4). One needs to be reminded, however, that in contrast to the measurement of  $R_{\text{ev}}$  presented above the observation of the change in ice film thickness addresses the net rate of evaporation and is therefore smaller than  $R_{\text{ev}}$  at a given partial pressure of  $\text{H}_2\text{O}$ .

The FTIR absorption spectroscopic study has led to four sets of results that have been obtained at 190 K on a  $1\ \mu\text{m}$  thick ice film and which are summarized in Table 3.

First, the spectrum of pure ice in Fig. 9 reveals the presence of polycrystalline  $I_h$  ice in the OH-stretch region as discussed previously. The spectrum shows an absorption peak at  $3230\ \text{cm}^{-1}$  with shoulders at  $3150$  and  $3350\ \text{cm}^{-1}$  (Bergren et al., 1978) which is expected from previous work on films deposited at temperatures higher than 180 K (Kumai, 1968). For a dose of less than  $10^{13}$  molecules of HCl deposited at a rate of less than  $10^{13}\ \text{molec s}^{-1}$  (Table 3, case a), no change in optical density was observed across the entire IR absorption spectrum from  $700$  to  $4000\ \text{cm}^{-1}$  which remained that of pure ice. However, the presence of HCl on ice was ascertained by the decrease of  $J_{\text{ev}}$  of  $\text{H}_2\text{O}$  as described above. For a dose of HCl of more than  $10^{14}$  molecules that is evaluated from the integral under the measured MS signal of HCl as displayed in Fig. 2 and a deposition rate of more than  $10^{14}\ \text{molec s}^{-1}$  (Table 3, case d) the formation of an amorphous HCl: $\text{H}_2\text{O}$  mixture was observed whose absorption spectrum is in agreement with results found in the literature (Dominé et al., 2001).

The obtained spectra for amorphous HCl: $\text{H}_2\text{O}$  mixtures are displayed in Fig. 10 and are in good agreement with the literature (Ritzhaupt et al., 1990). They are characterized by the appearance of new peaks between  $1100$  and  $1200$  as well as at  $1700\ \text{cm}^{-1}$  and by the broadening of the sharp OH-stretch band leading to a broad absorption around  $3250\ \text{cm}^{-1}$ . Ritzhaupt et al. (1990) have identified a stretching vibration of  $\text{H}_3\text{O}^+$  at  $1079\ \text{cm}^{-1}$  whereas  $\text{H}_2\text{O}$  bending and  $\text{H}_3\text{O}^+$  bond deformation modes con-

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tribute to the absorption at  $1696\text{ cm}^{-1}$  in their FTIR absorption spectra. Koch et al. (1997) attribute a  $1250\text{ cm}^{-1}$  band to the  $\text{H}_3\text{O}^+$  stretching mode and a  $1780\text{ cm}^{-1}$  vibration to the  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  deformation mode. We therefore follow these assignments in this work and identify the broad absorption band centered at approximately  $1100\text{ cm}^{-1}$  in Figs. 9 and 10 with the presence of  $\text{H}_3\text{O}^+$ . The sharp absorptions at  $1618$  and  $1644\text{ cm}^{-1}$  in the case of the  $\text{HCl}$  hexahydrate (Fig. 9) as well as the broader peaks centered at  $1640$  and  $1720\text{ cm}^{-1}$  in the case of the amorphous  $\text{HCl}:\text{H}_2\text{O}$  mixture (Fig. 10), whose IR bands are broadened throughout the IR absorption spectrum in line with the amorphous nature of the absorber, point to the activity of the bending and deformation modes in  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$ , respectively. Although no proof in itself, we claim that the significant intensity of these absorptions points towards the existence of ionic  $\text{HCl}$  hydrates of the form  $\text{H}_3\text{O}^+\text{Cl}^-$  being present on ice in the temperature range investigated as no hint of molecularly adsorbed  $\text{HCl}$  could be found in the region of the  $\text{H-Cl}$  stretching vibration.

The most interesting result of these deposition experiments is the ability to control the growth of the crystalline  $\text{HCl}$  hexahydrate  $\text{HCl}\cdot 6\text{H}_2\text{O}$  at  $190\text{ K}$  presented as cases (b) and (c) displayed in Table 3. Figure 9 presents a FTIR absorption spectrum corresponding to case (b), where the ice film was doped with  $10^{15}$   $\text{HCl}$  molecules at a flow rate of  $10^{13}\text{ molec s}^{-1}$ . The presence of crystalline  $\text{HCl}\cdot 6\text{H}_2\text{O}$  is characterized by the shift and split of the  $3230\text{ cm}^{-1}$  peak representative of the pure ice  $\text{OH-stretch}$ , and by the appearance of sharp peaks at  $1644\text{ cm}^{-1}$  and  $1618\text{ cm}^{-1}$  discussed above (Ritzhaupt et al., 1990). Similar to case (d) of Table 3, the spectrum of Fig. 9 corresponding to the deposition conditions of case (b) displayed in Table 3 reveals the formation of a crystalline ionic hydrate of  $\text{HCl}$  with ice in agreement with the literature (Koch et al., 1997; Uras-Aytemiz et al., 2001) and with theoretical studies (Kroes et al., 1992; Gertner et al., 1996; Svanberg et al., 2000). We point out that this spectrum has been measured at a time in the film evaporation history that corresponds to the time interval given by points **B** and **D** of the interferogram displayed in Fig. 3 where all of the free water molecules constituting the underlying pure ice film have evaporated.

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This explains the importance of the FTIR absorptions attributed to the presence of the hydrates compared to the pure ice OH-stretch around  $3250\text{ cm}^{-1}$  as all other  $\text{H}_2\text{O}$  molecules not involved in crystalline hydrate formation have evaporated leaving behind the “bare essentials” of the stable crystalline hydrate. The fact that the (almost) unperturbed ice OH-stretch at  $3244$  and  $3264\text{ cm}^{-1}$  (compared to  $3250\text{ cm}^{-1}$  in pure ice) is still observable at this stage of the evaporation attests to the presence of weakly-bound water molecules not involved in the formation of the hydrates although both their rate of evaporation and condensation are influenced by the presence of HCl as indicated by their slight shift in the IR absorption spectrum.

The results are consistant with fact that HCl hydrates have a  $\text{H}_2\text{O}$  vapor pressure that is lower than that of pure ice although it has not been mesasured in this work. It is also important to notice that the IR absorption peaks corresponding to the presence of HCl hydrates were also observable down to a coverage of  $5 \cdot 10^{13}$  molecules of HCl towards the end of an evaporation experiment. This HCl dose corresponds to approximately 10% of a formal monolayer of HCl on ice. At the beginning of the evaporation experiment the crystalline hydrate structure was not apparent perhaps because of the abundance of “pure” ice whose absorption spectrum is centered at  $3250\text{ cm}^{-1}$  (Fig. 9). After most of the ice film evaporated at the rate characteristic of pure ice the remaining sample was monitored using the disappearance of the spectral fingerprints of the hydrates as given in Fig. 9. At this time it had an average mole fraction of HCl in ice between  $1.6 \cdot 10^{-4}$  and  $3.2 \cdot 10^{-4}$  as indicated by the volume of remaining ice monitored by the interferogram for the time period between **C** and **D** of Fig. 3. We are unable at this point to determine the defining moments of the crystallization of the HCl hexahydrate. If it crystallized already at the end of the doping process the sensitivity of the FTIR absorption spectrometer in transmission may not have been sufficient to monitor the characteristic features of the crystalline HCl hexahydrate at  $3549$ ,  $3471$  and  $3409\text{ cm}^{-1}$ . On the other hand, crystallization as probed by the appearance of the sharp hydrate structure in the OH-stretching region may have occurred when most of the pure ice had evaporated and the HCl concurrently concentrated at the interface thus en-

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abling crystallization. This process would resemble closely the crystallization of nitric acid hydrates ( $\text{NAT} = 3\text{H}_2\text{O}\cdot\text{HNO}_3$ ,  $\text{NAD} = 2\text{H}_2\text{O}\cdot\text{HNO}_3$ ) under laboratory conditions as observed by Tolbert and coworkers (Zondlo et al., 2000).

5 A surprising case is (c) in Table 3 which indicates the absence of crystalline  $\text{HCl}\cdot 6\text{H}_2\text{O}$  and reveals that the formation of the crystalline hexahydrate depends on the rate of HCl deposition rather than on the HCl dose. For very low deposition rates of less than  $10^{13} \text{ molec s}^{-1}$  one concludes that the diffusion of HCl in ice is presumably faster than crystallization preventing the formation of the HCl hexahydrate. At the other  
10 extreme of a large deposition rate (case (d) in Table 3) formation of an amorphous  $\text{HCl}\cdot\text{H}_2\text{O}$  mixture is preferred over formation of crystalline hexahydrate. Whatever the reason, it seems that at 190K both the crystalline and amorphous HCl hydrates may be observed depending on the rate of deposition of HCl on ice. This case is of importance because the change in the net rate of evaporation seems to depend on the presence or absence of crystalline hydrates as displayed in Table 2, cases (c) and (b'). More  
15 importantly, the formation of these crystalline hydrates observed by FTIR absorption spectroscopy has a large impact on the rate of  $\text{H}_2\text{O}$  evaporation for a sample comprising the last 100 to 200 nanometers of ice whereas in the case of the formation of an amorphous  $\text{HCl}\cdot\text{H}_2\text{O}$  this impact is less which may be an indication of the importance of diffusion of HCl in the formation of the crystalline hydrates. Table 2 qualitatively shows  
20 the difference of the impact of the presence of  $\text{HCl}\cdot 6\text{H}_2\text{O}$  (case (b')) vs. amorphous  $\text{HCl}\cdot\text{H}_2\text{O}$  mixture (case (c)) as far as the temporal spacing between the interference fringes which are related to the evaporation rate of  $\text{H}_2\text{O}$  are concerned.

For ice films doped with HBr, we have not been able to observe any spectral changes in the pure ice spectrum except for a broadening of the absorption due to the OH-stretch region and a shift of the  $1641 \text{ cm}^{-1}$  peak as displayed in Fig. 11 (Koehler et al., 1993). This is assigned to the bending mode of  $\text{H}_2\text{O}$  which is shifted to  $1745 \text{ cm}^{-1}$   
25 upon HBr adsorption and is attributed to the  $\text{H}_3\text{O}^+$  bending mode. This observation suggests complete ionization of HBr and is in agreement with the literature (Barone et al., 1999; Hudson et al., 2001). However, similar to the case of HCl, where no spectral

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change was observed (case a, Table 3) the presence of HBr was ascertained by the measurement of the decrease of  $J_{\text{ev}}$  of  $\text{H}_2\text{O}$ , as presented in Fig. 4.

#### 4. Discussion and atmospheric implications

This experiment has enabled the separation of the rate of evaporation  $R_{\text{ev}}$  or  $J_{\text{ev}}$  and the rate constant for condensation  $k_{\text{cond}}$  of  $\text{H}_2\text{O}$  from pure and doped water ice under the same experimental conditions. The separate rates and especially their temperature dependence have shed light on a complex adsorption/desorption mechanism as evidenced by the negative temperature dependence of  $k_{\text{cond}}$  as has been pointed out by Flückiger et al. (2003). The resulting value for the enthalpy of sublimation of  $\text{H}_2\text{O}$  from pure water ice deduced from Arrhenius expressions given above is  $\Delta H_{\text{subl}} = E_{\text{ev}} - E_{\text{cond}} = 11.9 \pm 2.7 \text{ kcal mol}^{-1}$  which is in good agreement with values found in the literature (Haynes et al, 1992; Fraser et al, 2001, Koehler, 2001). In contrast to most other results found in the literature, we assert that  $\text{H}_2\text{O}$  condensation on ice has a small negative activation energy in the range studied (190–240 K). The study of  $R_{\text{ev}}$  alone is therefore a necessary, but not sufficient condition to assess  $\Delta H_{\text{subl}}$  or the binding energy of  $\text{H}_2\text{O}$  on ice at temperatures in excess of 190K, as has been repeatedly done in the past (Haynes et al., 1992). For HCl-doped ice  $\Delta H_{\text{subl}} = 11.2 \pm 2.8$  and for HBr-doped ice  $\Delta H_{\text{subl}} = 11.7 \pm 2.8 \text{ kcal mol}^{-1}$ , the latter of which is in good agreement with Hudson et al., 2001.  $\Delta H_{\text{subl}}$  is independent of the presence of HX in the given concentration range and equal to  $\Delta H_{\text{subl}}(\text{pure ice})$  within experimental uncertainty in agreement with the  $\text{H}_2\text{O}$  vapor pressure being that of ice even for the HX-doped ice samples. However, a small counterintuitive decrease of  $E_{\text{ev}}$  may be noted in the sequence pure ice>HCl/ice>HBr/ice which is offset by a counteracting preexponential factor. The constant value of  $\Delta H_{\text{subl}}$  is consistent with the fact that the vapor pressure of  $\text{H}_2\text{O}$  is independent of the amount of adsorbed HX in the range between  $10^{13}$  and  $10^{15}$  molecules deposited on a  $0.78 \text{ cm}^2$  ice film. These conditions lead to low concentrations of [HX] in our experiments with an upper limit for

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$\chi_{\text{HCl}} = 1.2 \cdot 10^{-2}$  which is valid in the case of an ice sample a few tens of nanometers thick corresponding to point **E** of the interferogram and displayed in Fig. 3.

The unexpected stability of the vapor pressure of  $\text{H}_2\text{O}$  above the ice film in the presence of HCl follows the observation made in previous experiments concerning the prolongation of the lifetime of ice particles due to NAT-coating (Biermann et al., 1998) in which no change of the  $\text{H}_2\text{O}$  vapor pressure was observed. However, Biermann et al. report the observation of the net rate of evaporation of pure ice and NAT/ice films and conclude that both rates are identical within experimental error which differs from our conclusions on  $R_{\text{ev}}$  and  $k_{\text{cond}}$  on pure, HCl- and HBr-doped ice. Their work also leads to  $\text{H}_2\text{O}$  mass accommodation coefficients that are in the range 0.025 to 0.05 which is at least an order of magnitude smaller than recent measurements on ice, including our work (Chaix et al. 1998; Flückiger et al. 2003). Most likely transport limitations of  $\text{H}_2\text{O}$  owing to the used high total pressure corresponding to a mbar or so led to these results at variance with all other experiments to date.

In our work, the decrease of the pre-exponential factor of the rate of evaporation of water from ice by 2 and 3 orders of magnitude for HCl and HBr, respectively, is consistent with previous results found in the literature (Hudson et al., 2001) and represents the most significant effect of HX on ice evaporation and thus on the lifetime of atmospheric ice particles. The observation of the negative temperature dependence of  $k_{\text{cond}}$  implies the presence of a surface-bound precursor for adsorption, hence a complex adsorption/desorption mechanism as has been discussed in the literature (Chaix et al., 1998; Flückiger et al., 2003). The decrease of both  $R_{\text{ev}}$  and  $k_{\text{cond}}$  in the presence of HX therefore may imply a modification of the ice surface at atmospherically relevant conditions. Indeed, cases (b) and (c) of Table 3 lead to an average mole fraction of HCl in a 1  $\mu\text{m}$  thick ice film of  $\chi_{\text{HCl}} = 2$  to  $4 \cdot 10^{-5}$  for  $5 \cdot 10^{13}$  to  $1 \cdot 10^{14}$  adsorbed HCl molecules. These concentrations represent lower limits and may be higher by at most a factor of four if one allows for the evaporation of 50 and 75% of the pure ice in the sample that is not affected by the presence of HCl as displayed in Table 2 for the amorphous and crystalline HCl hydrate, respectively.

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In most cases the modification of the ice is observable by FTIR spectroscopy as displayed in Fig. 9 and 10 and clearly shows the importance of the deposition conditions, even for atmospheric conditions according to the results displayed in Table 3. Type II polar stratospheric (ice) clouds have been found on occasion in stratospheric air much warmer than the ice frost point  $T_{ice}$ . A particularly pertinent observation has been made by Deshler et al. from a balloon-borne sounding of arctic stratospheric air when large ice particles with radii in the range 1–5  $\mu\text{m}$  have been observed surviving for hours at temperatures several degrees (3–10) above  $T_{ice}$ . These observations and others (Goodman et al., 1997) have led to the hypothesis that a NAT coating around the ice particle prevented rapid evaporation of ice that would occur on the time scale of a few minutes in the absence of the NAT coating. In light of the present results it may be asked whether the existence of a crystalline NAT coating may be required for the decrease of the evaporation rate of  $\text{H}_2\text{O}$  or if simply the presence of adsorbed  $\text{HNO}_3$ , perhaps as amorphous  $\text{HNO}_3/\text{H}_2\text{O}$  mixture (Zondlo et al., 2000) may already be a sufficient requirement. This hypothesis begs the question as to the mole fraction or absolute concentration of  $\text{HNO}_3$  required to lead to an effective decrease of the net evaporation rate.

The significant effect of HX deposition on  $R_{ev}$  from ice may also be seen in HeNe interferograms shown in Fig. 3 and summarized in Table 2, and has been observed in two other studies of the condensed phase, one for HBr (Hudson et al., 2001), the other for HCl (Krieger et al., 2002). Our values for HBr are consistent with those in the literature (Hudson et al., 2001) and may lead to a surprising increase of the lifetime for an ice particle. For HCl, Krieger et al. report a decrease of the net rate of evaporation of  $\text{H}_2\text{O}$  from ice of only 30%, whereas we observe a decrease of a factor of 5 to 6 depending on the structure of the HCl/ice surface. The increase of the lifetime of a 1  $\mu\text{m}$  thick ice film in the presence of HX may be extrapolated to the case of Cirrus clouds. As Cirrus cloud particles are large they may be approximated by bulk substrates so that the results obtained in this study may be transferable to the case of PSC's type II such that HX-doped ice particles should have an increased lifetime in the presence of HX

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depending on the amount of HCl adsorbed. They should thus be more available for heterogeneous reactions and so be more efficient in ozone depletion processes as discussed in Solomon et al., 1997.

The results displayed in Fig. 4 that are expressed in the Arrhenius expressions given above for H<sub>2</sub>O evaporation from pure ice and ice contaminated by adsorbed HX amount to a decrease of R<sub>evap</sub> and k<sub>cond</sub> by a factor of 5 to 6 and 15 for HCl and HBr adsorption in the indicated concentration and temperature range, respectively. These results have been obtained under conditions of molecular flow in the interest of separating the individual rates of equilibrium (3) and correspond to a relative humidity rh of a fraction of a percent. However, owing to the fact that the measured equilibrium vapor pressure of H<sub>2</sub>O does not change upon adsorption of HX the decrease in R<sub>evap</sub> and k<sub>cond</sub> is independent of relative humidity rh because the net evaporation  $\Delta R_N = k_{\text{cond}}[H_2O](rh-1)$  is a linear function of rh and affects the net evaporation of pure ice and ice contaminated with HX to the same extent. Therefore, the ratio r of the net rate of H<sub>2</sub>O evaporation from pure ice compared to HX doped ice given in Eq. (5) and the relative decrease f of the net rate of H<sub>2</sub>O evaporation upon doping of ice with HX displayed in Eq. (6) are independent of the relative humidity rh.

$$r = k_{\text{cond}}^{\text{HX}}/k_{\text{cond}} = R_{\text{ev}}^{\text{HX}}/R_{\text{ev}} \quad (5)$$

$$f = (k_{\text{cond}}^{\text{HX}} - k_{\text{cond}})/k_{\text{cond}} = (R_{\text{ev}}^{\text{HX}} - R_{\text{ev}})/R_{\text{ev}}, \quad (6)$$

where the symbols with the superscripts correspond to the kinetic constants pertaining to HX doped ice samples.

## Annex A: The partial pressure of H<sub>2</sub>O over ice measured in a chamber at ambient temperature and under molecular flow conditions

A) The partial pressure of H<sub>2</sub>O over ice, P<sub>H<sub>2</sub>O</sub>, at typically 200 K measured in a vessel of the same temperature T is identical to the equilibrium vapor pressure P<sub>eq</sub>. In such a

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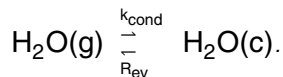
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system the one temperature of the condensed phase as well as the chamber walls control  $P_{eq}$ . The corresponding  $H_2O$  concentration,  $[H_2O]$ , is equal to the molecular density given by Eqs. (7) and (8) when either the rate ( $R_{ev}$ ) or the flux ( $J_{ev}$ ) of condensation and evaporation of  $H_2O$  in the presence of ice, respectively, are expressed in terms of true chemical equilibrium between the  $H_2O$  gas and condensed phase, namely



$$R_{ev} = \gamma \omega [H_2O] \quad \text{with} \quad \omega = \langle c(T) \rangle \frac{A_s}{4V} \quad (7)$$

$$J_{ev} = \gamma \frac{\langle c(T) \rangle}{4} [H_2O] \quad \text{with} \quad R_{ev} = J_{ev} \frac{A_s}{V} \quad (8)$$

In Eqs. (7) and (8)  $\gamma$ ,  $\omega$ ,  $\langle c(T) \rangle$ ,  $A_s$  and  $V$  are the uptake coefficient, the gas-surface collision frequency, the mean molecular velocity, the geometrical area of the substrate and the volume of the reaction system, respectively.

**B)** In practice, however,  $P_{H_2O}$  and  $[H_2O]$  are measured in an experimental system where the condensed phase is at low temperature and whose walls are at ambient temperature. In this case the condensed phase at low temperature ( $T_L$ ) and the chamber walls at ambient temperature ( $T_H$ ) both control  $P_{H_2O}$  and  $[H_2O]$ , both of which do not correspond to the equilibrium vapor pressure  $P_{eq}$  and the equilibrium  $H_2O$  concentration,  $[H_2O]$ , respectively. The former situation A) corresponds to true equilibrium between the cold target and the cold chamber walls without ambiguity, except that this is a hypothetical situation rarely encountered in performed experiments. Conversely, the often encountered situation B) implies that collisions of gas at ambient temperature  $T_H$  (hot gas) occur with a target (ice) at  $T_L$  in which case  $P_{H_2O}$  and  $[H_2O]$  are given by two temperatures  $T_H$  and  $T_L$ . The measured partial pressure of  $H_2O$ ,  $P_{meas}$ , and the measured concentration of  $H_2O$ ,  $[H_2O]_{meas}$ , may be calculated by postulating that the

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equilibrium conditions given in Eqs. (9) and (10) hold thus implying no net growth or loss of the quantity of the condensed phase at  $T_L$ .

$$J_{ev} = \gamma \frac{\langle c(T_L) \rangle}{4} [H_2O] = \gamma \frac{\langle c(T_H) \rangle}{4} [H_2O]_{meas} \quad (9)$$

$$J_{ev} = \gamma \frac{\langle c(T_L) \rangle}{4} \frac{P_{eq}}{RT_L} = \gamma \frac{\langle c(T_H) \rangle}{4} \frac{P_{meas}}{RT_H} \quad (10)$$

5 This means that the constraint of no net change of the quantity of the condensed phase adjusts the measured values of  $P_{H_2O}$  and  $[H_2O]$  according to Eqs. (11) and (12) corresponding to an apparent equilibrium measured under realistic experimental conditions.

$$[H_2O]_{meas} = [H_2O] \left( \frac{T_L}{T_H} \right)^{1/2} \quad (11)$$

$$10 \quad P_{meas} = P_{eq} \left( \frac{T_H}{T_L} \right)^{1/2} \quad (12)$$

Equations (11) and (12) show that both  $T_L$  and  $T_H$  control the measured experimental quantities  $P_{meas}$  and  $[H_2O]_{meas}$ . Equations (7) and (8) imply that for  $T_L < T_H$ ,  $[H_2O]_{meas} < [H_2O]$ , the equilibrium concentration of  $H_2O$  at  $T_L$ , and  $P_{meas} > P_{eq}$ , the true equilibrium vapor pressure at  $T_L$ . In the hypothetical case that the rate constant for  $H_2O$  condensation,  $(\gamma)(\omega)$ , were independent of temperature,  $[H_2O]_{meas} = [H_2O]$  and  $P_{meas} = P_{eq} \bullet (T_H/T_L)$  would result as expected.

15 *Acknowledgements.* Generous support of this research was granted by the Fonds National Suisse de la Recherche Scientifique under contract 20-65299.01 and in part by OFES under the 5<sup>th</sup> framework project CUTICE of the European Union under the Environnement and Climate Program.

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**Table 1.** Data on experimental hardware configuration and results of calibrations. The sample surface area is  $A_s=0.78 \text{ cm}^2$

Experiment configuration	Reactor Temperature [K]	Reactor Volume [cm <sup>3</sup> ]	Collision frequency on ice [s <sup>-1</sup> ]		Rate of effusion for calibrated leak [s <sup>-1</sup> ]		Calculated escape orifice [mm <sup>2</sup> ]	HeNe angle [degree]	Thickness for one HeNe fringe [nm]	Thickness for FTIR OD=1.08 [nm]	MS Calibration factor [molec s <sup>-1</sup> A <sup>-1</sup> ]	
			H <sub>2</sub> O	HCl	H <sub>2</sub> O	HCl					H <sub>2</sub> O	HCl
1	300	1750	6.52	4.62	0.2	0.13	2.4	12	246	1000	$5.80 \cdot 10^{24}$	$6.31 \cdot 10^{24}$
2	330	2450	4.89	3.46	0.055	0.043	0.8	12	246	1000	$5.70 \cdot 10^{23}$	$6.25 \cdot 10^{23}$

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**Table 2.** Experimental observations of the HeNe interferogram during the evaporation of a 1 μm thick pure ice film, as well as doped with HCl, under stirred flow conditions and for different doping conditions. Cases (a), (b), (c) correspond to experimental configuration 1 (Table 1), cases (a') and (b') to configuration 2 (Table 1)

Ice Substrate Temperature [K]	Ice Thickness at deposition time [nm]	Dose of HCl molecules	Rate of deposition [molec s <sup>-1</sup> ]	Time for complete film evaporation [s]	Last 4 periods between fringes [s]				Trapped H <sub>2</sub> O molecules	FTIR Spectral characterization at fringe 4
					1	2	3	4		
(a) 180	1000	Pure Ice	Null	217	67	60	50	40	Null	Pure Ice
(b) 180	1000	1 · 10 <sup>15</sup>	1 · 10 <sup>13</sup>	320	74	69	58	116	1.5 · 10 <sup>18</sup>	HCl·6H <sub>2</sub> O
(c) 190	1000	1 · 10 <sup>15</sup>	6 · 10 <sup>12</sup>	450	73	75	120	160	1.5 · 10 <sup>18</sup>	Amorphous HCl:H <sub>2</sub> O
(a') 190	1000	Pure Ice	Null	125	30	30	30	35	Null	Pure Ice
(b') 190	1000	1 · 10 <sup>15</sup>	1 · 10 <sup>13</sup>	708	35	35	38	600	1.5 · 10 <sup>18</sup>	HCl·6H <sub>2</sub> O

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**Table 3.** FTIR spectral observations of a 1  $\mu\text{m}$  thick ice film doped with HCl using different dosing protocols at 190 K

	<i>a)</i>	<i>b)</i>	<i>c)</i>	<i>d)</i>
Dose (molecule)	Low $< 10^{13}$	$5 \cdot 10^{13}$ to $10^{15}$	$5 \cdot 10^{13}$ to $10^{15}$	$> 10^{14}$
Flow rate (molec s $^{-1}$ )	Low $< 10^{13}$	$10^{13}$ to $5 \cdot 10^{13}$	Low $< 10^{13}$	Large $> 10^{14}$
Spectral observation	No absorption attributable to HCl	$3250 \text{ cm}^{-1}$ Split+ shift  Sharp 1644 and $1618 \text{ cm}^{-1}$	$3250 \text{ cm}^{-1}$ broadening  1100 and $1700 \text{ cm}^{-1}$ absorption	$3250 \text{ cm}^{-1}$ broadening  1100 and $1700 \text{ cm}^{-1}$ absorption
Identification	FTIR absorption spectrum is that of pure ice	Crystalline HCl hexahydrate (Fig. 9)	Amorphous HCl:H $_2$ O mixture (Fig. 10)	Amorphous HCl:H $_2$ O mixture (Fig. 10)

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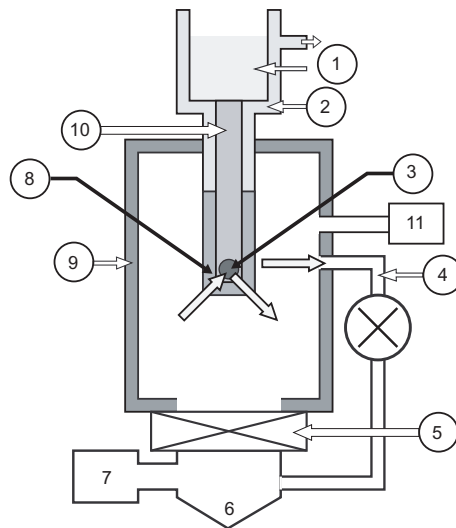
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**Fig. 1.** Schematic drawing of the experiment: **1** Liquid nitrogen reservoir, **2** Evacuated Dewar vessel, **3** Silicon window of  $0.78 \text{ cm}^2$  area used as a substrate for  $\text{H}_2\text{O}$  deposition, **4** Calibrated leak equipped with a valve allowing static (valve closed) and stirred flow (valve open) experiments, **5** 6" diameter gate valve, **6** Flange for Turbo Pump, **7** Quadrupole Mass spectrometer, **8** PTFE thermal insulation isolating the whole cryostat but the Silicon window which is the only low temperature part exposed to the gas phase, **9** Reactor chamber, **10** Solid copper finger with cartridge heaters for heating used to control the temperature of the Silicon Substrate, **11** Absolute pressure gauge (Baratron). Several type T thermocouples (not shown here) are located throughout the vacuum side of the cryostat in order to measure the temperature in different areas (Silicon window, PTFE Insulation, Reactor and Calibrated Leak walls,...). In addition, two 2" diameter NaCl windows allow the FTIR monitoring of the condensed phase, and two inlets allow the injection of  $\text{H}_2\text{O}$  as well as HX into the reactor. The hollow arrows describe the important kinetic processes taking place, such as adsorption, desorption and effusion of  $\text{H}_2\text{O}$  vapor.

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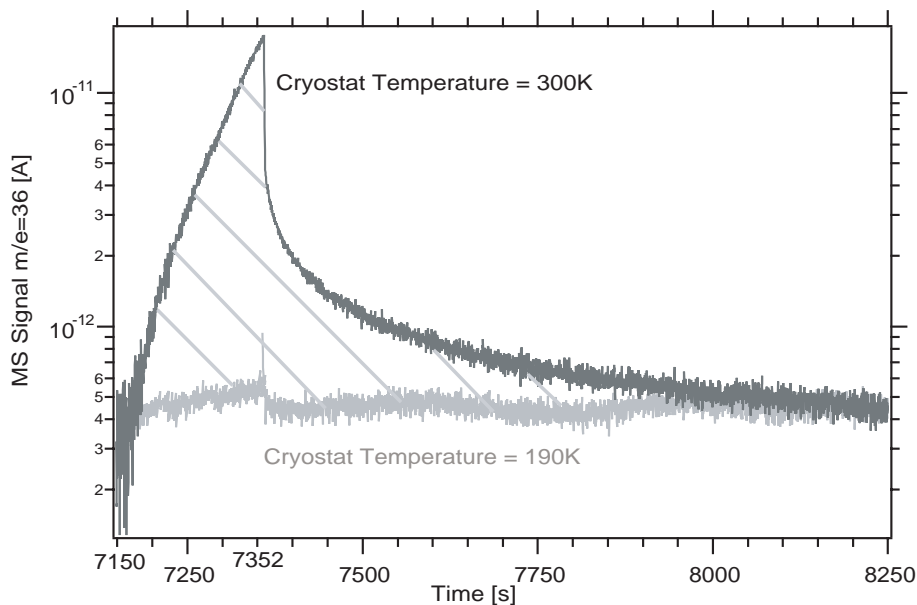
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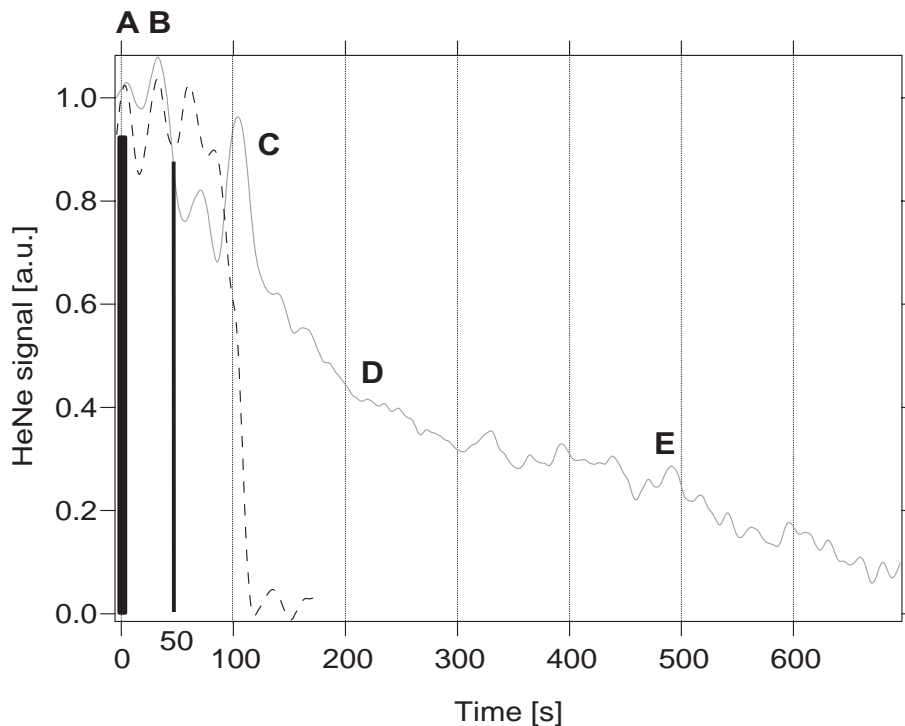
**Fig. 2.** Raw mass spectrometer signal for HCl at  $m/e=36$ . The black and grey traces correspond to the reference signal with the cryostat at 300 K and 190 K in the presence of ice, respectively. At  $t=7150$  s, the HCl dosing valve is opened to the same extent in both cases, and is closed at  $t=7352$  s. In this example the total amount of HCl molecules disappearing from the gas phase is  $(8 \pm 0.5) \cdot 10^{14}$  molecules and corresponds to the hatched area.

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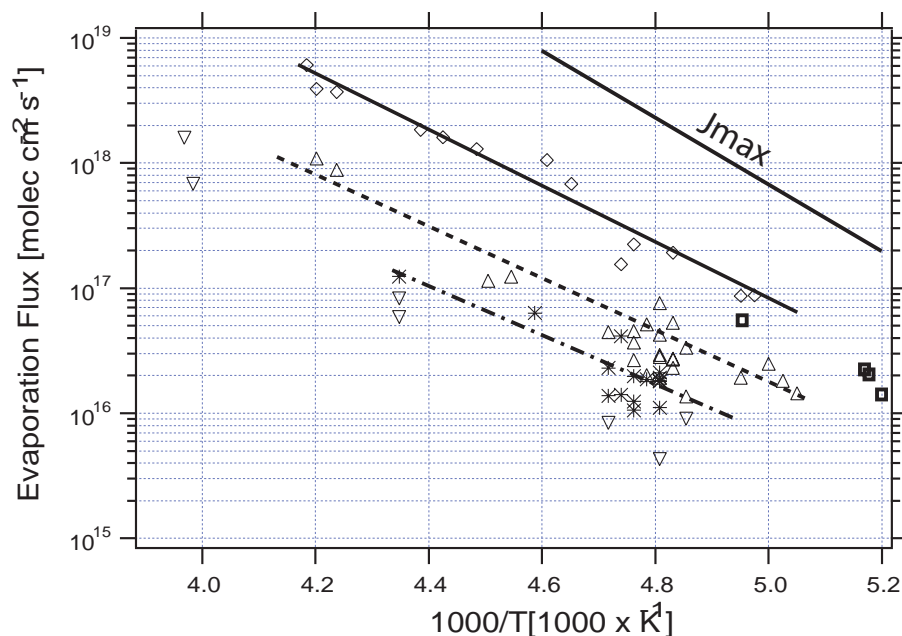


**Fig. 3.** Interferometric signal of evaporating: **(a)** pure ice (black dashed), **(b)** HCl-doped ice film of  $10^{15}$  deposited HCl at 190 K (gray). At  $t=0$ , the static system is set to stirred flow condition by opening the leak valve (First black vertical line). The second vertical line corresponds to the first noticeable difference between interferograms.

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**Fig. 4.** Arrhenius plot of the evaporative flux of  $\text{H}_2\text{O}$  ( $J_{\text{ev}}$ ) from pure and HX doped ice films ( $\square$ : condensed ice, Chaix et al., 1998;  $\diamond$ : condensed ice, this work;  $\triangle$ : HCl-doped ice, this work;  $*$ : HBr-doped ice, this work). The typical uncertainty of individual points are within the size of the symbols.  $\nabla$ : value observed for a very large dose of HCl leading to the formation of a liquid HCl/ $\text{H}_2\text{O}$  mixture on the ice surface.  $J_{\text{max}}$  corresponds to the theoretical maximum value for the evaporative flux of a pure ice film ( $\gamma=1$ ).

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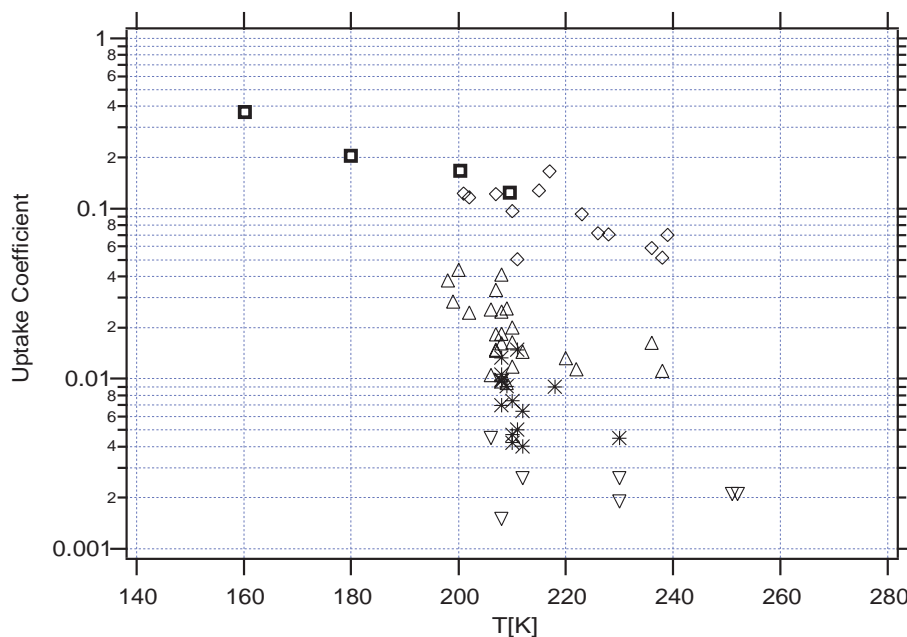
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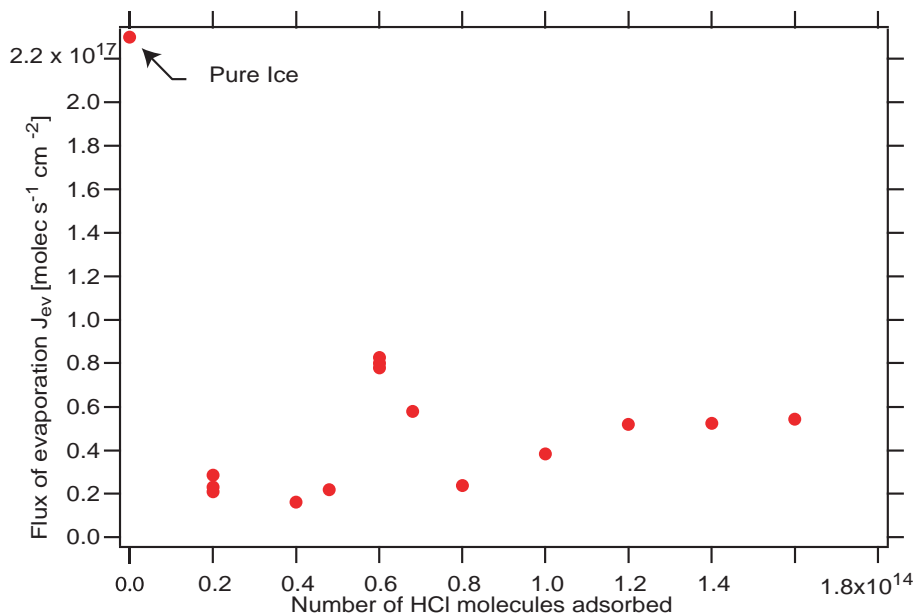


**Fig. 5.** Temperature dependence of the uptake coefficient  $\gamma$  of  $\text{H}_2\text{O}$  from pure and HX-doped ice films ( $\square$ : condensed ice, Chaix et al., 1998;  $\diamond$ : condensed ice, this work;  $\Delta$ : HCl-doped ice, this work;  $*$ : HBr-doped ice, this work.  $\nabla$ : value observed for a very large dose of HCl leading to the formation of a liquid HCl/ $\text{H}_2\text{O}$  mixture on the ice surface.)

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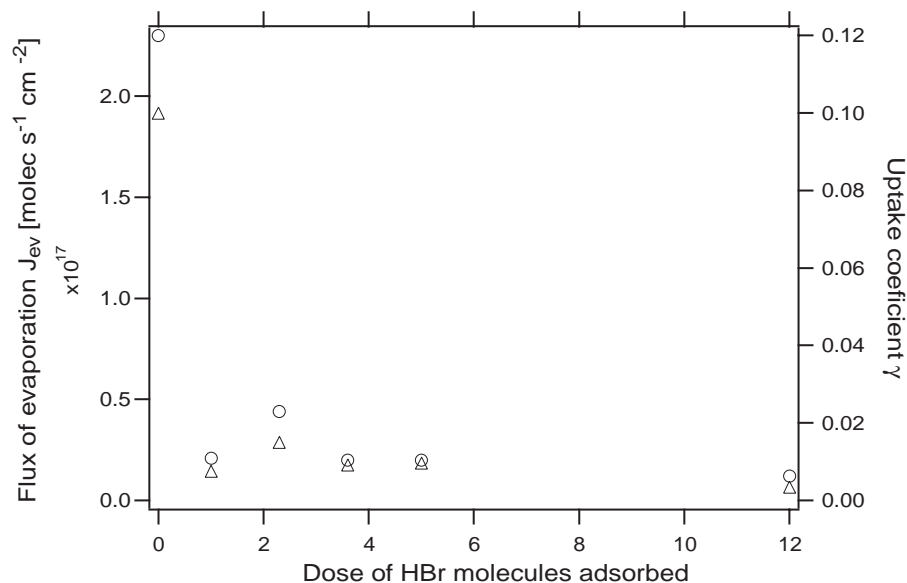


**Fig. 6.** Dependence of  $J_{ev}$  on the number of HCl molecules adsorbed on  $0.78\text{cm}^2$  of ice substrate at 210 K. The stable level appearing for a dose higher than  $1 \cdot 10^{14}$  molecules was chosen for the data displayed in Figure 4.

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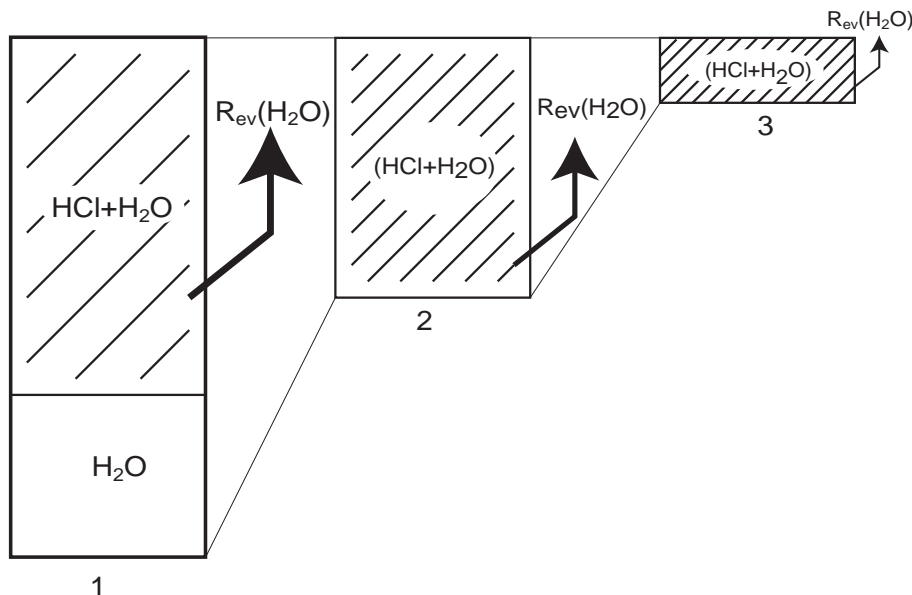


**Fig. 7.** Dependence of  $J_{ev}$  ( $\circ$ ) and  $\gamma$  ( $\Delta$ ) on the number of HBr molecules adsorbed on the ice surface at 210K. The stable level for a dose higher than 3.6 was used in Figure 4. A dose of 1 corresponds to a maximum of  $5 \cdot 10^{16}$  molecules adsorbed but due to the experimental setup it was impossible to get quantitative values for HBr.

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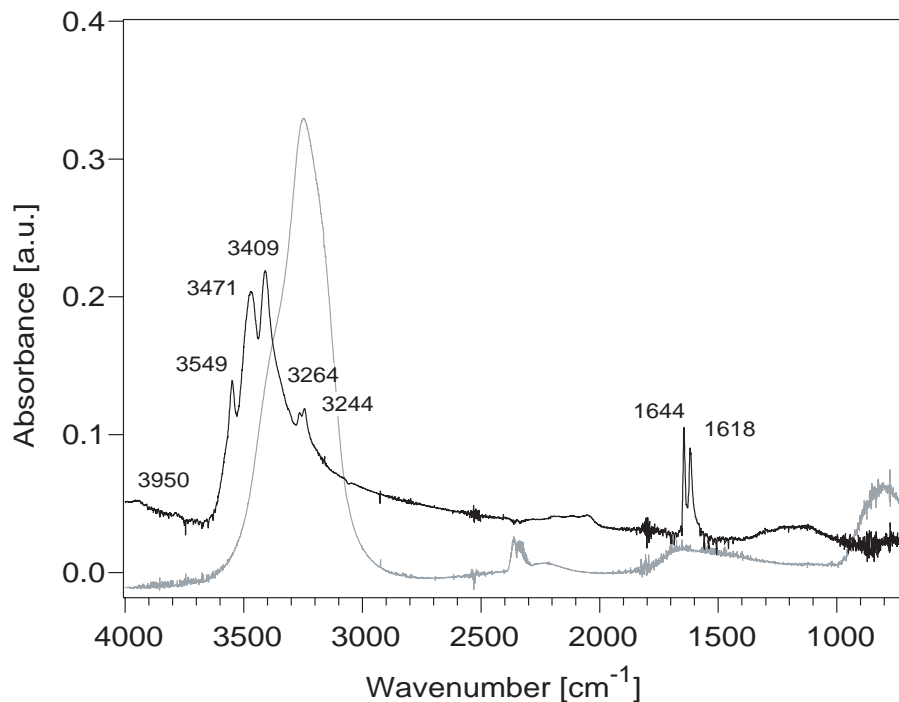


**Fig. 8.** Cartoon of the fate of a HCl-doped ice film upon evaporation of  $\text{H}_2\text{O}$  (see text for explanation). Hatched areas represents the mixture of  $\text{HCl}/\text{H}_2\text{O}$ .

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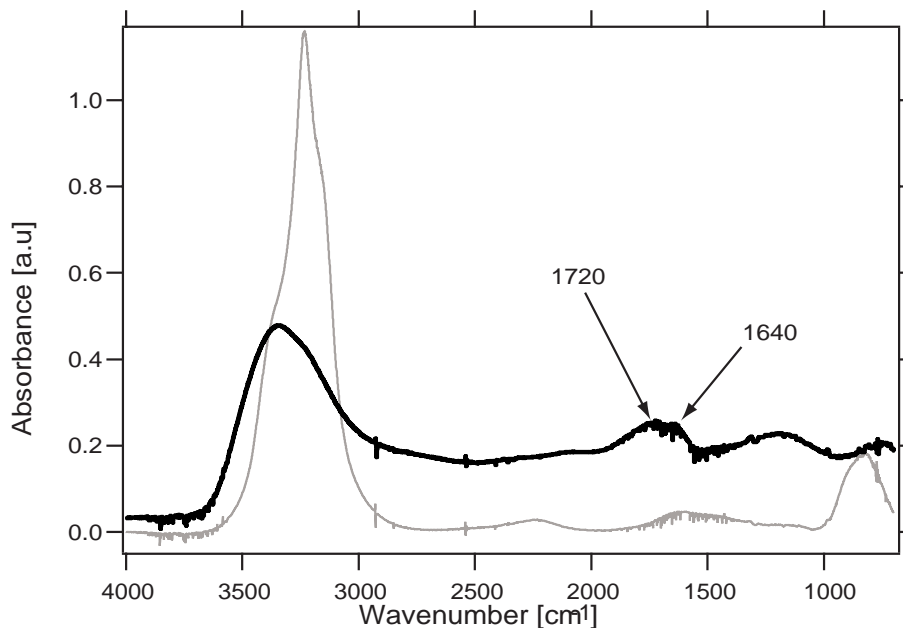


**Fig. 9.** FTIR absorption spectrum of pure (grey) and HCl-doped ice (black). Both traces are rescaled for legibility. The ice film is doped with  $10^{15}$  molecules of HCl at a flow rate of  $10^{13}$  molec s<sup>-1</sup>.

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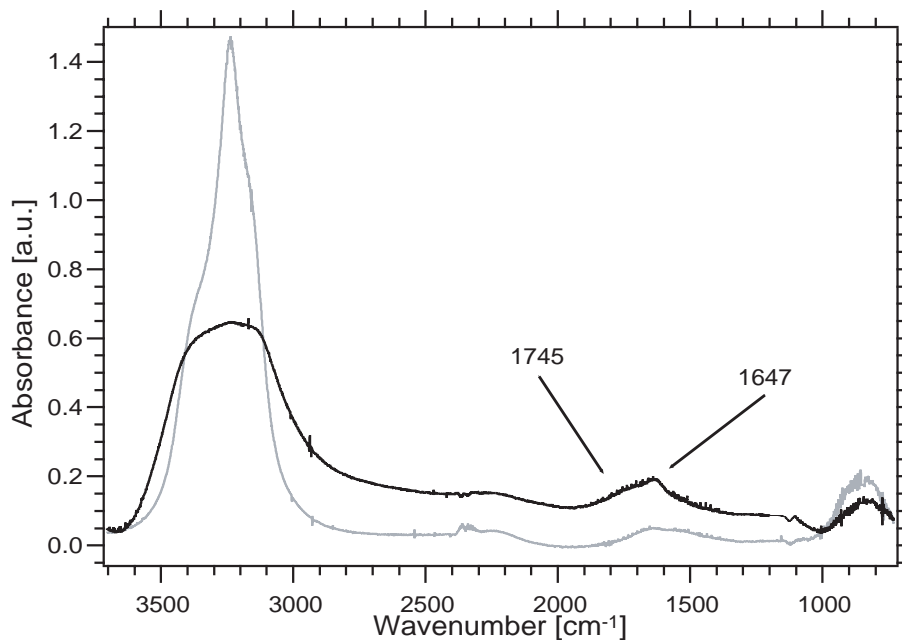
**Fig. 10.** FTIR absorption spectrum of pure (grey) and HCl-doped ice (black). Both traces are rescaled for legibility. The ice film is doped with  $10^{15}$  molecules of HCl at a flow rate higher than  $10^{14}$  molec s $^{-1}$ .

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**Rate of water vapor  
evaporation from ice  
substrates in the  
presence of HCl and  
HBr**

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**Fig. 11.** FTIR absorption spectrum of pure (grey) and HBr-doped ice (black). Both traces are rescaled for legibility. The ice film is doped with an unknown amount of HBr.

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